

Production of Propylene from Steam Cracking of Hydrocarbons, Particularly Ethan

The present invention relates to a method of producing 5 propylene from a hydrocarbon feed stream involving the steam cracking of the hydrocarbon and then processing the ethylene that is produced to produce the propylene. The invention is particularly applicable to a feed stream which is all or mostly ethane.

10 **Background of the Invention**

Propylene has grown in importance and it now has the second highest worldwide production rate in the petrochemical industry. Propylene has a variety of downstream uses such as polypropylene and propylene oxide and the demand is expected to grow at rates of 15 5% to 6% each year. Therefore, new, lower-cost routes to propylene production are of high interest in the petrochemical marketplace. Today the majority of propylene is produced either as a principal byproduct in steam cracking units, which primarily produce ethylene, or as a byproduct from fluid catalytic cracking units, which 20 primarily produce gasoline. Both the steam cracker and the fluid catalytic cracking unit require naphtha as a feedstock to make significant quantities of propylene product although lesser amounts of propylene can be produced by feeding propane or butane to the steam cracking unit. While gasoline demand remains strong, ethylene 25 demand is expected to grow at an annual rate of only 3% to 4%, below the growth rate in propylene. In addition, much of the new steam cracker capacity will be based on using ethane as a feedstock. Using ethane as a feedstock to a steam cracker typically produces only ethylene as a final product. While hydrocarbons heavier than 30 ethylene are present, typically the quantities are too small to warrant recovery and there is essentially no propylene produced. These two

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factors, the higher growth rate of propylene product demand and the reduced quantity of co-produced propylene from new steam cracker units, have and will manifest themselves in a shortage of the supply of propylene and higher propylene product values.

5 The primary reason many of the new steam cracking units are using ethane as a feedstock is because ethane is a co-product of natural gas production and has limited value for uses other than as a feedstock to a steam cracker unit. As natural gas demand and production rates grow for supplying electrical power and home
10 heating needs, ethane availability increases beyond its regional demand. Since ethane cannot be readily or economically transported, regional demand is important and where its availability exceeds regional demand, its price is reduced. In many regions, ethane feed costs are 25% to 50% of other steam cracker feedstocks such as
15 propane, butane or naphtha. This gives a large advantage to producing ethylene using low cost ethane feedstock. In addition, energy costs and capital investments for a steam cracker using ethane feedstock are far below the costs for using propane, butane or naphtha as a feedstock.

20 One commercial operation does produce polymer grade propylene by producing butene from polymer grade ethylene in a dimerization plant and then using the formed butene to react with additional polymer grade ethylene to form the polymer grade propylene in a metathesis plant. However, that operation uses a
25 liquid feedstock which is cracked to produce both ethylene and propylene with the propylene production only being supplemented by the conversion of polymer grade ethylene to propylene. That operation does not involve the cracking of a fresh ethane feedstock to produce ethylene and then using the ethylene in metathesis and
30 dimerization reactions as the only source of propylene. The ability to produce propylene using ethane feedstock is currently not practiced commercially.

The ability to effectively produce propylene using ethane, or mostly ethane, feedstock would significantly lower feedstock costs, energy costs and required capital investment just as it does for the production of ethylene. Providing a route for propylene production from ethane feedstock would also better utilize the available ethane feedstock. As noted above, the only current utilization for the ethane co-produced in natural gas production is to use it as a feedstock for ethylene production which raises concerns about an oversupply of ethylene product and the impact that would have on ethylene pricing and demand. Hence, some producers do not utilize all the available ethane. Providing a route to produce propylene from ethane feedstocks would help ensure that ethane utilization is high in all regions.

15 Summary of the Invention

The object of the present invention is to provide an improved, more economical method for producing propylene from a hydrocarbon feedstock. The invention in its broadest form involves the steam cracking of the hydrocarbon feedstock to produce an ethylene-containing stream which is processed in an ethylene plant recovery section including a C₂ fractionator to obtain polymer and/or chemical grade ethylene and ethane for recycle. The ethylene is then reacted by metathesis with butene to produce propylene product. In one embodiment of the invention when the hydrocarbon feedstock is other than pure or mostly ethane, chemical grade ethylene is processed by metathesis to produce the propylene and the purge gases from the metathesis are processed in the ethylene plant recovery section, preferably in the C₂ fractionator.

In another embodiment of the invention, the hydrocarbon feedstock is either pure ethane or mostly ethane. In this embodiment, a portion of ethylene from the C₂ fractionator is processed by dimerization to produce butene and another portion of

the ethylene is reacted by metathesis with that butene to produce the propylene product. The ethylene plant recovery section, the dimerization section and the metathesis section are all integrated for the handling of the purge and other process streams.

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Brief Description of the Drawings

Figure 1 is a process flow scheme showing a conventional prior art process involving the steam cracking of ethane to produce an ethylene product.

10 Figure 2 is a process flow scheme illustrating one embodiment of the present invention involving the steam cracking of ethane to produce a propylene product.

Figure 3 is a process flow scheme similar to Figure 2 but illustrating a variation of the process.

15 Figure 4 is a process flow scheme illustrating a further variation of the invention.

Figure 5 is a process flow scheme similar to Figure 3 but eliminating the dimerization section.

20 Figure 6 is a process scheme similar to Figure 4 but eliminating the dimerization section.

Detailed Description of the Invention

The production of ethylene from ethane feedstock in a steam cracking unit is widely practiced. Figure 1 illustrates such a conventional steam cracker process using ethane as the sole feedstock. The fresh ethane feed 10, typically obtained by separation from natural gas, and a recycle ethane stream 12 are fed to a cracking heater 14 where, in the presence of steam, the ethane is heated with the resulting formation of ethylene and hydrogen as primary products and the formation of methane, C₃ and heavier hydrocarbons as secondary products. Ethane once-through conversion varies between 50 and 80%, with most commercial

plants operating in the 60 - 75% conversion region. The steam cracker effluent is then treated in the ethylene plant recovery section where it is first cooled at 16 and then compressed at 18. At 20 the compressed stream is then chilled to separate hydrocarbon

5 condensates from light gases 22 such as hydrogen and CO and the hydrocarbon condensates are demethanized to separate out methane 24. The demethanizer bottoms 26 flow to a deethanizer 28 where C₃ and heavier hydrocarbons are separated in the bottoms 30 and C₂ hydrocarbons are recovered the overhead 32. The deethanizer

10 overhead 32 is then selectively hydrogenated at 34 to convert acetylene to ethylene after which the C₂ mixture flows to a C₂ fractionator 36.

In the C₂ fractionator 36, polymer-grade ethylene is typically taken as the overhead product 38 and an ethane rich stream 12 is

15 taken as the bottom product. The ethane rich bottom product 12 is recycled back to the cracking heaters 14. The polymer grade ethylene can be taken as a direct overhead product or, alternately, it could be withdrawn as a side product a few separation stages down from the top of a fractionation tower, with the top trays then

20 functioning as a pasteurization section to concentrate light gases such as hydrogen and methane in a small vent gas stream taken overhead.

In most of these prior art ethane crackers, the C₃ and heavier hydrocarbons are not recovered as chemical products but rather

25 utilized as fuel products. This is because the quantity of these compounds is low in a pure ethane cracker. In a very large ethane cracking plant, or in an ethane cracking plant which also cracks propane, then it may be economical to recover propylene, and perhaps, also other heavier products for chemical use. But typically,

30 the recovered non-fuel products heavier than ethylene are still made in low quantities.

In one embodiment of the present invention, a steam cracker for ethane or primarily ethane (defined as 70% or more ethane) is designed to produce ethylene. The ethylene is recovered and some is dimerized to butene. Then the produced butene is reacted with 5 additional ethylene recovered from the steam cracker to produce propylene. Thus, an ethane cracker based complex can produce both ethylene and propylene products. Within the context of the overall process flow schemes, several process integrations are possible to improve economics.

10 Figure 2 illustrates a first embodiment of the invention wherein the fresh ethane or primarily ethane feed 40 and the recycle ethane stream 42 are cracked, cooled and compressed at 44. The compressed stream containing the ethylene, hydrogen, methane and C₃ and heavier hydrocarbons, just as in the prior art illustrated in 15 Figure 1, is then chilled and demethanized at 46 removing light gases 48 and methane 50. The demethanizer bottoms are then deethanized at 52 where the C₃ and heavier hydrocarbons 54 are separated. The deethanizer overhead is then selectively hydrogenated at 56 to convert the acetylene primarily to ethylene. The C₂ mixture is then 20 fractionated at 58 to separate the ethane recycle 42 and the ethylene product 60. Although not shown, the C₂ fractionator 58 would have a typical reboiler and overhead condenser and separator to produce reflux. The demethanizer 46, deethanizer 52 and the C₂ fractionator 58 are referred to as the ethylene plant recovery section. As an 25 option for this ethylene plant recovery section, the deethanizer may be first, followed by the acetylene hydrogenation unit and then followed by the demethanizer. The demethanizer bottoms would then flow to the C₂ fractionator 58. The ethylene product 60 is then split with a portion 62 going to the dimerization reaction 64 and the 30 other portion 66 going to the metathesis reaction 68.

The ability to produce propylene, by reacting butene and ethylene is something that, while not widely practiced commercially,

is known to the industry. This process route utilizes a chemistry called olefins metathesis. Fresh ethylene 66 and recycled ethylene 70 and butenes 72, from the dimerization reaction 64 to be described, flow to the metathesis reactor 68 where they react to 5 form an equilibrium mixture of propylene, ethylene and butenes, as well as small quantities of C₅ and heavier olefins. Ethylene conversion is typically below 50% per pass. The metathesis reaction including the temperatures, pressures and catalysts are well known in the art. The reactor effluent 74 flows to a deethanizer 75 wherein 10 C₂'s are taken overhead at 76 and the C₃ and heavier hydrocarbons are in the bottoms product. Most of the C₂'s form the recycle 70 back to the reactor 68. A small purge 80 is taken to limit the buildup of inerts, chiefly ethane. The deethanizer bottoms 78 flows to a depropanizer 82 where the final polymer-grade propylene is distilled 15 overhead at 84. Two bottoms products are usually taken. One is a side-stream 86 containing mostly butenes which is recycled back to the metathesis reactor 68. A bottoms stream 87 is also taken as a purge to limit the buildup of inerts, chiefly n-butane, and also to reject the C₅'s and heavier products formed in the reactor.

20 The ability to produce butene, either butene-1 or butene-2, by reacting ethylene with itself is also known to the industry and is called dimerization. Dimerization of ethylene to preferentially produce butene-2 is practiced commercially and is used in the present invention as a source of the feedstock for metathesis. The butene-2 25 is reacted in the presence of a catalyst with ethylene to form propylene. The conversion of the ethylene is less than 100% and typically about 80% or greater. The effluent 90 from the dimerization reactor 64 flows to the deethanizer 92 wherein unreacted ethylene and ethane in the overhead 94 are separated from 30 the butene in the bottoms 96. The overhead 94 is mostly recycled at 98 back to the reactor 64 and a small purge 100 is withdrawn to again control the buildup of inerts, chiefly ethane. The deethanizer

bottoms 96 flows to a butene separation 88 where the product butene 72 and a purge stream 102 are withdrawn. The product 72 then goes to the metathesis reaction 68 for the production of the propylene. The purges 80 and 100 from the deethanizers 75 and 92 5 can be recycled back to the recovery section of the ethylene plant, i.e., back to the demethanizer 46 or deethanizer 52 or preferably to the C₂ fractionator 58. Alternately, they can be recycled back to the charge gas compressor, although this is less preferable.

Figure 3 illustrates another embodiment of the invention which 10 uses a lower purity, chemical grade ethylene for dimerization and metathesis. Polymer grade ethylene has a purity usually above 99%, typically 99.5% plus, or more typically, 99.9% plus, whereas this embodiment of the invention uses chemical grade ethylene which is less than 99% pure and typically from 90 to 95% pure with the 15 balance being essentially ethane. The chemical grade ethylene product 60 is now withdrawn as a side stream from a lower tray in the C₂ fractionator 58. Polymer-grade ethylene stream 61 may also be withdrawn as a source of ethylene for polymer production.

The advantage of using lower purity ethylene is a reduction in 20 the capital cost and the operating cost of the ethylene plant complex. The separation of ethylene and ethane is capital and energy-intensive. It is more economical to produce a lower purity, chemical grade ethylene product and then convert some of this contained ethylene to butenes in the dimerization section and to propylene in the 25 metathesis section. The resulting ethylene-ethane mixture is then upgraded to a chemical-grade purity.

In this Figure 3 embodiment, there is an integration between the dimerization, metathesis and ethylene plant sections. The lower purity, chemical grade ethylene is utilized for both the dimerization 30 and metathesis reactions. Unconverted ethylene and contained ethane from both of these reactions are recycled, directly or indirectly, back to the recovery section of the ethylene plant,

preferably back to the C₂ fractionator or less preferably to the deethanizer or demethanizer.

The butene product 90 from the dimerization reaction 64 containing the unreacted ethylene and the contained ethane is fed 5 directly to the butene separation 88 rather than to a deethanizer as in Figure 2. Unconverted C₂'s are recovered in the butene separator overhead by being co-absorbed in the fresh and recycle C₄'s to the metathesis reactor, eliminating the need for the deethanizer 92 as in Figure 2. The depropanizer, 82, would produce a propylene product, 10 84, as in Figure 2 and a single bottom product, 86. The bottom product from the depropanizer 82, containing mostly butenes as well as other butane and heavier hydrocarbons, is then fed to the butene separation 88. The purge stream 102 is removed and the combined product butene 72 is fed to the metathesis reaction 68. The 15 propylene-containing metathesis effluent 74 flows to the deethanizer 75 where the remaining C₂'s from both the dimerization and metathesis reactions are removed in the overhead 76. The overhead is cooled and partially condensed at 104 and separated at 106 to provide the reflux 108.

20 The net overhead 110 is preferably returned to the C₂ fractionator 58. The net overhead 110 enters the C₂ fractionator 58 at a stage that is not necessarily the same as the feed from the steam cracking plant, allowing for more efficient operation of this tower. The recycle ethylene flow back to the reactor is then the 25 same purity as the chemical grade ethylene product. No buildup of ethane occurs, leading to a higher partial pressure of ethylene in the reactors, at a constant reactor operating pressure. No separate purge of inerts from the reactor loops is required. Rather, the inerts are purged as essentially pure ethane from the bottom of the C₂ fractionator, limiting the losses of ethylene. The use of this process 30 feature could also result in a lower metathesis reactor operating pressure. The reflux ratio and stripping section heat input for the

deethanizer 75 are reduced if the C₂ separation tower can be operated at lower pressure. Refrigeration is required but this can be provided by the refrigeration system present in the ethylene plant in a separate overhead condenser at an appropriate tower pressure and 5 refrigeration temperature level.

Alternately, especially when using chemical grade ethylene, the deethanizer 75 may be fully integrated with the ethylene fractionator 58 and operated at the same pressure. No separate condenser, separator drum or reflux pumps are needed. This is shown in Figure 10 4 which is a total integration rather than the partial integration as introduced in Figure 3. In this concept, the deethanizer in the metathesis unit does not have an overhead system to produce reflux. Rather, the total overhead of this tower system flows directly to the C₂ fractionator. The chemical grade product from the C₂ fractionator 15 then provides both the fresh feed and the recycle to the metathesis reactors and also provides the reflux to separate the C₂ stream from heavier streams in the metathesis section deethanizer. Clearly, there will be fewer pieces of process equipment required for the Figure 4 process scheme versus Figure 3. The total energy consumption and 20 the total capital cost of the two process schemes will depend upon the specifics of the process, as practiced in a particular design. Both process schemes, however, are a clear improvement over the prior art, utilizing polymer grade ethylene and with no direct integration with the ethylene fractionator. In prior art metathesis plants, the 25 deethanizer has operated at approximately 400 psi, with cooling of the overhead provided by propylene refrigeration, typically operating at approximately -20°F to +10°F level. In the Figure 4 embodiment of the invention, this deethanizer 75 can be operated at the same pressure as the C₂ fractionator 58. The total overhead vapor 76 30 flows to the C₂ fractionator. Reflux 112 to the deethanizer is a portion of the total chemical grade ethylene 60 from the C₂ fractionator.

The main commercial markets for this integrated process are believed to be ethane steam cracking to make polymer-grade ethylene and polymer grade propylene products. However, the integrations between the ethylene fractionator and the metathesis plants are 5 applicable to olefin plants, irrespective of feedstock utilized. Two integration concepts between the steam cracker, the ethylene plant recovery section and the dimerization and metathesis section deethanizers are taught and both of these inventive concepts are applicable to the integration of ethylene plants and metathesis plants 10 whatever the feedstock to the steam cracker and whatever the process configuration of the steam cracker.

If there is a substantial amount of cracking of propane and heavier, it is possible, and practiced commercially, to have the depropanizer as the first hydrocarbon removal tower. Often the 15 acetylene hydrogenation unit is located on the overhead of the depropanizer when this process configuration is utilized. The depropanizer overhead would then flow to either a demethanizer or deethanizer. If the second hydrocarbon removal tower is a demethanizer, then the demethanizer bottoms would flow to a deethanizer and the deethanizer overhead would flow to a C₂ 20 fractionator. The concepts of the present invention would also apply to this process configuration. Similarly, the depropanizer overhead could flow to a deethanizer, then the deethanizer overhead to a demethanizer. The demethanizer bottoms would then flow to a C₂ 25 fractionator. The concepts of the present invention would also apply to this process configuration.

The invention, in either the partial or total integration modes, enables the dimerization and metathesis units to operate at relatively high concentration of ethylene in their reaction loops while only 30 providing chemical-grade purity ethylene rather than polymer-grade purity ethylene. In the total integration mode, it also enables deethanization in the metathesis plant to be carried out at a much

lower pressure and potentially with fewer equipment items. In the metathesis area, this lower pressure deethanization further enables the metathesis reaction itself to proceed at a lower pressure, decreasing equipment costs.

5 In the invention as depicted in Figures 3 and 4, no direct recycle from the deethanizer 75 in the metathesis section to the metathesis reactor 68 is practiced. Unconverted ethylene is processed in the ethylene plant ethylene fractionator 58 and chemical-grade ethylene is recycled to the reactors. In practice, for
10 the Figure 3 embodiment, it is possible to send some of the unconverted ethylene recovered from the overhead of the metathesis plant deethanizer 75 to the metathesis and dimerization reactors and the balance of the ethylene recycle sent to processing in the C₂ fractionator 58.

15 The drawings show an ethylene fractionator 58 which would have a pasteurization section above the main rectification section and all products are produced as side streams. It is also possible to utilize a secondary demethanizer instead of a pasteurization section to separate lights. In this operation, the overhead of the ethylene fractionator, as a liquid, flows to the secondary demethanizer, which is typically a stripping column. Light gases plus associated ethylene are withdrawn overhead and the bottoms is the polymer-grade ethylene product. The overhead can be recycled back to a low pressure demethanizer for recovery of C₂'s or alternately, to the
20 25 charge gas compressor of the ethylene plant.

 In a plant with a front end deethanizer or front end depropanizer, neither a pasteurization section or secondary demethanizer may be required. The partial or total integration concepts between the C₂ fractionator and the dimerization and
30 metathesis sections would still apply, however. The invention, with minor detail changes, is thus applicable whatever the fundamental

process flow configuration of the steam cracker might be and is also applicable whatever cracking feedstock might be utilized.

The combination of processing steps of the present invention provides a unique route to propylene production from ethane or 5 primarily ethane feedstocks. This route is a much lower cost production route for propylene (1) because of the use of lower cost ethane feedstocks relative to the propane, butane, naphtha or gas oil feedstocks used in steam cracking units or the heavy oil feedstocks used in fluidized catalytic cracking units; (2) because it consumes 10 less energy than propylene production from steam crackers; and (3) because it has a lower capital investment, for a given polymer grade propylene production than either heavy feed steam crackers or fluidized catalytic cracking units. It also produces lower greenhouse gas emissions and therefore is a more environmentally friendly route.

15 The use of chemical grade ethylene from a steam cracker and using metathesis and dimerization have been discussed above. These concepts are also applicable to steam-cracking plants operated with any hydrocarbon feedstock. For example, it is possible with a mixed ethane/propane feedstock with less than 70% ethane or even a 20 propane feedstock to utilize both dimerization and metathesis to increase propylene production. For butane and heavier hydrocarbon feeds to the steam cracker, and for most steam crackers which utilize propane feedstock, economics favor the use of by-product cracked C₄'s to be the source of butenes for metathesis. Thus, these plants 25 will not need an ethylene dimerization section. Only the steam cracking plant with the ethylene plant recovery section and the metathesis section will be required. The recovery of butene from cracked C₄ streams and other process steps available to produce butene suitable as the source of the butene for the metathesis are 30 well known to those skilled in the art. The integration steps taught in Figures 3 and 4, however, are novel and can be utilized for this plant configuration as well.

Figure 5 depicts the integration concepts taught in Figure 3 when utilized in a steam cracker plant with a metathesis section to increase propylene production. The feedstock to the steam cracker can be any hydrocarbon, from ethane to vacuum gas oil. Ethylene fractionator 58 produces a polymer-grade product 61 and a chemical-grade product 60. The chemical grade product flows to the metathesis reaction section 68 along with fresh butene feedstock 63 and a recycle butenes stream 86. The source 65 of the fresh butene stream 63 could be derived from the unsaturated C₄'s present in stream 54 and/or potentially other unsaturated C₄'s such as refinery off-gas streams or catalytic dehydrogenation streams. Stream 74 exits the metathesis reaction section 68 and is composed of an equilibrium or near equilibrium mixture of propylene, ethylene and butenes along with mostly-paraffin inerts and a small quantity of C₅'s and heavier. This stream then flows to the deethanizer and is processed as described for the Figure 3 configuration. The net overhead 110 is returned back to the ethylene fractionator 58 in the ethylene plant recovery system. No separate recycle of ethylene to the metathesis reaction section 68 is typically practiced as was indicated by stream 70 in Figure 2. Rather, the metathesis reaction is operated once through in ethylene flow. The deethanizer bottoms 78 flows to the depropanizer 82. Polymer-grade propylene is taken off as stream 84 and, when combined with the propylene recovered from stream 54, would clearly increase the total propylene production in the plant. Recycle C₄'s are removed as a side stream 86 near the bottom of the fractionating section of the depropanizer and sent to the metathesis section 68 as previously described. A purge stream 87 is taken from the bottom of the depropanizer to remove C₅'s and heavier and to limit butane concentration buildup.

The advantage of the integration concept is a decrease in operating and capital costs for the total plant, as compared to using polymer-grade ethylene as the feed to the metathesis section. It is

less capital intensive and more efficient to produce chemical-grade than polymer-grade ethylene. However, with chemical-grade ethylene, ethane concentration can build up in the metathesis section, if recycled directly back from the deethanizer to the 5 metathesis reaction section. This integration enables the use of chemical-grade ethylene while avoiding ethane concentration buildup.

Similarly, Figure 6 depicts the integration concepts taught in Figure 4 when utilized in a system with only a metathesis section to increase propylene production. Fresh feed 40 to the cracking section 10 can be any typically utilized steam cracker feedstock from ethane to vacuum gas oil. The processing steps in the ethylene plant recovery section up to the ethylene fractionator are as previously described and generally known to those skilled in the art. The ethylene fractionator 58 produces a chemical-grade ethylene stream 60 which 15 flows to the metathesis reaction section 68. Here again, it is combined with fresh butene feedstock 63 and a recycle butene stream 86. Exiting the metathesis reactor, stream 74 flows to the deethanizer 75, wherein C₂'s are taken overhead as stream 76. This stream flows directly to the C₂ fractionator 58. The deethanizer has 20 no overhead condenser. Rather, stream 112 taken from the chemical-grade ethylene side draw steam 60 from the C₂ fractionator 58 provides reflux to the deethanizer 75. The deethanizer bottom stream, 78, flows to the depropanizer 82, and the subsequent processing is similar to that described for Figure 5.

25 The advantage of this process scheme is lower capital and lower operating costs for the total plant as compared to utilizing polymer-grade ethylene to feed the metathesis plant. There is a savings in required equipment items as compared to the Figure 5 scheme which also utilizes chemical-grade ethylene and the capital 30 cost of this scheme should be lower than for the Figure 5 scheme.